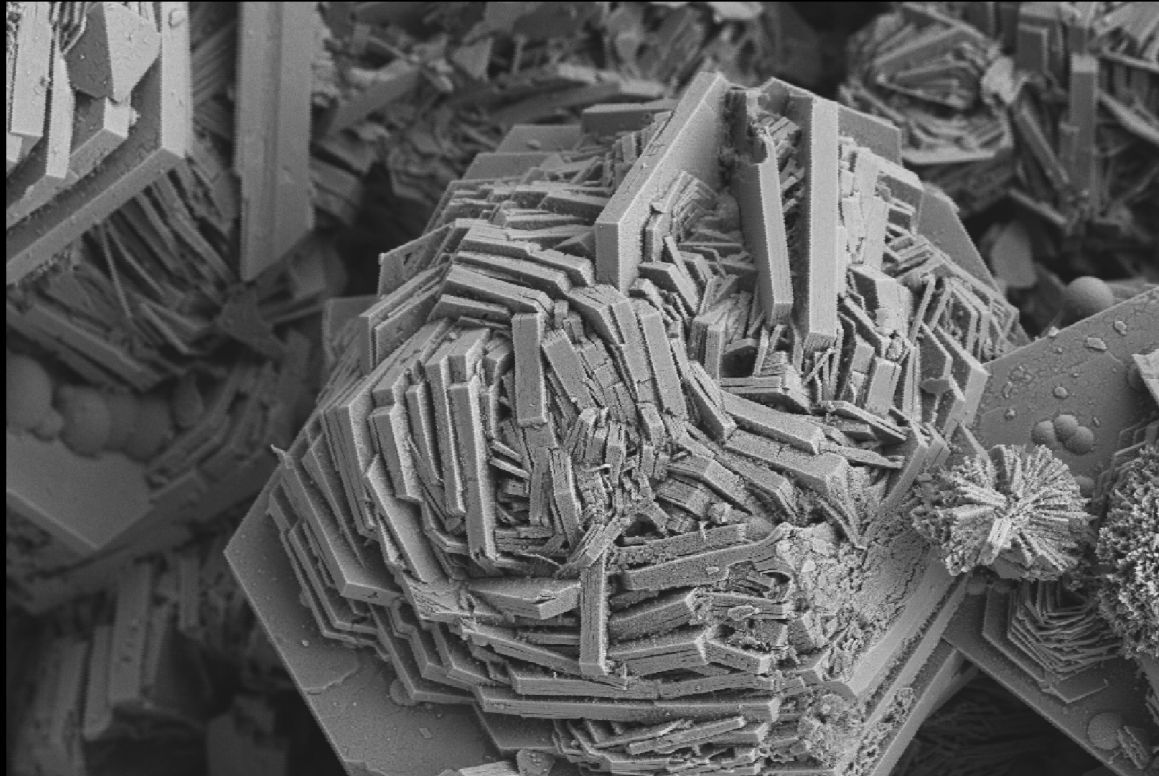


# ***Habitability in Saline Environments on Mars***



***Nicholas J. Tosca***

***Origins of Life Initiative***

***Organismic & Evolutionary Biology***

***Harvard University***

***Cambridge, MA 02138***





# The Ancient Martian Surface: How Habitable?



- **To what extent can we generalize?**
  - On Mars, like Earth, water is the only game in town...
- **Some controls on the limits of terrestrial life:**
  - Temperature
  - Radiation
  - Acidity
  - Temporal availability of water
  - **Salinity (water activity)**
- **Define habitability in an *evolutionary* context**
  - Prebiotic chemistry & the *origin* of life
  - Evolution and/or adaptation to changing surface chemistry



# Water Activity ( $a_{H_2O}$ )

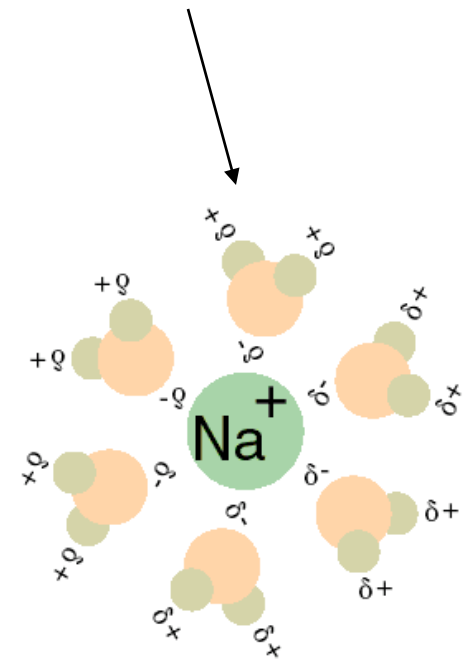


- **A thermodynamic measure of salinity**
  - Water is **chemically unavailable** at high solute concentration
  - Increasing salinity decreases water activity

$$\ln a_{H_2O} = \frac{\phi(\sum v_i m_i) M_w}{-1000}$$

## *Selected Water Activity Values*

Pure water	1.00
Average river water	0.99
Seawater	0.98
Halite (NaCl) saturation	0.75



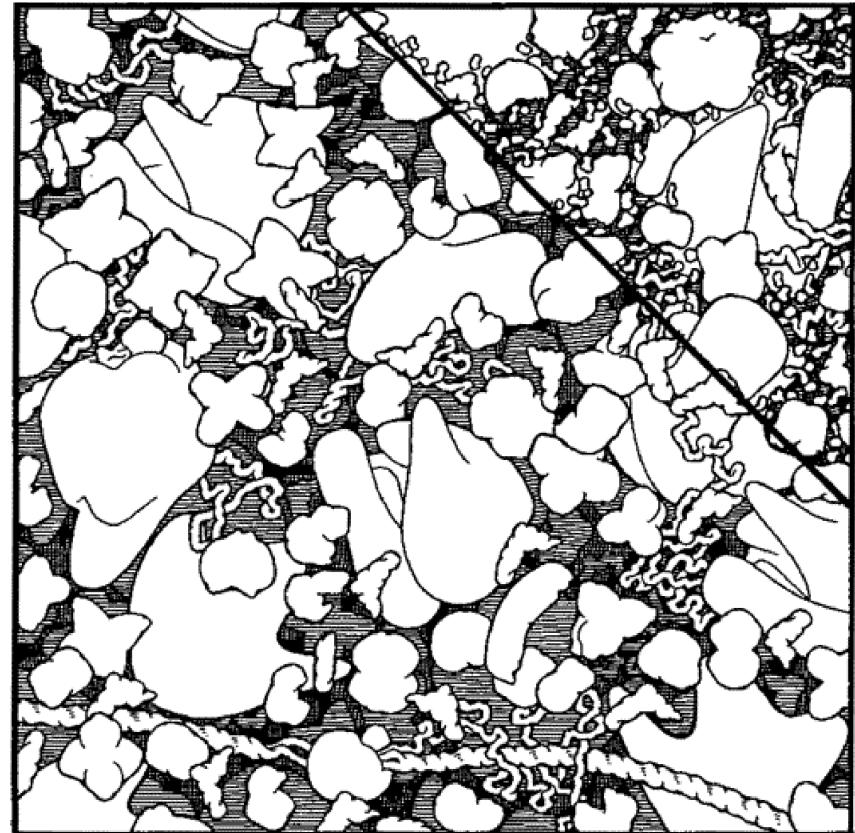
- **Sharp  $a_{H_2O}$  limitations on biological activity**



# $a_{\text{H}_2\text{O}}$ : Limits on terrestrial life



- **Microbial strategies for low  $a_{\text{H}_2\text{O}}$  conditions:**
  1. Synthesize “compatible solutes” (e.g., glycine, betaine)
  2. Increase salt content of cytoplasm  
*(Evolutionary processes)*
- **Biochemical consequences of high salinity (low  $a_{\text{H}_2\text{O}}$ )**
  - Inhibition of protein folding
  - Bio-molecule denaturation & functionality loss
- **What are the numerical limits?**



*Cytoplasm*, from Goodsell (1993) *The Machinery of Life*.





# $a_{\text{H}_2\text{O}}$ : Limits on terrestrial life



$a_{\text{H}_2\text{O}} \sim 0.90$ :

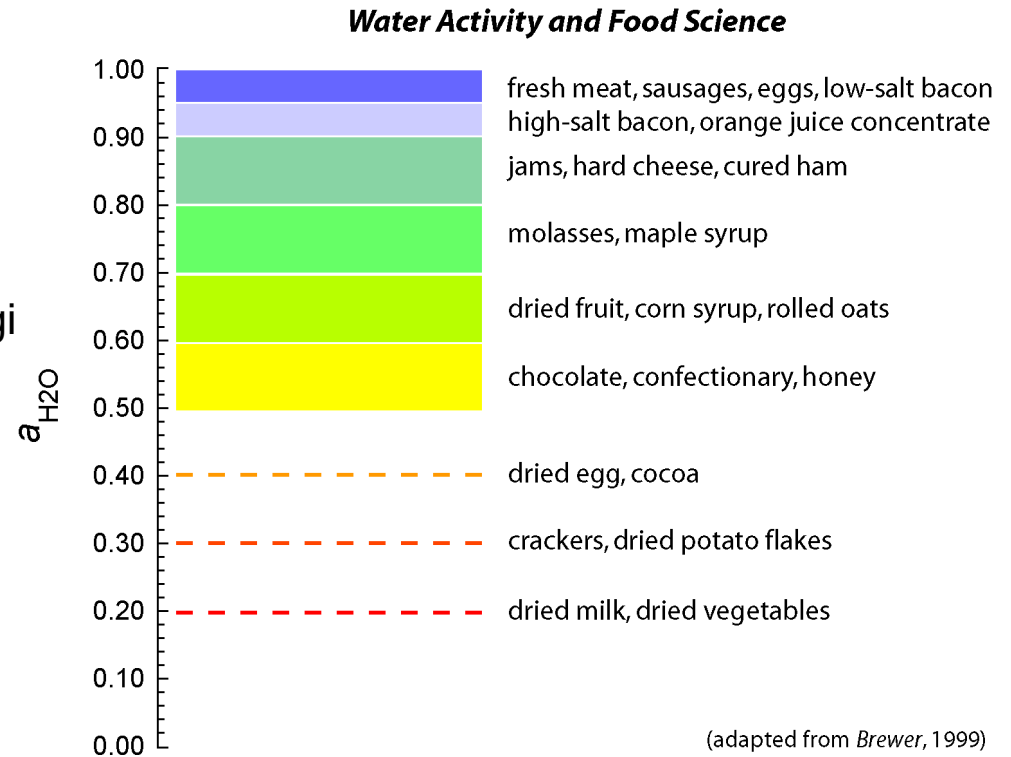
- Limit for most organism growth

$a_{\text{H}_2\text{O}} \sim 0.75$ :

- Limit for most extremophilic fungi & archaea

$a_{\text{H}_2\text{O}} = 0.61$ :

- Effective habitability limit
- *X. Bisporus* in high-sugar food



- $\sim 175$  of  $10^7$  known species exhibit halo-tolerance / halo-philism
- **Regardless of the precise number, limits provide useful benchmarks**



# Calculating $a_{H_2O}$ for Martian Systems



## 1. Constraints on dilute fluid chemistry

- Experimental weathering studies

## 2. Thermodynamic model for highly saline waters

## 3. Data on mineral solubility

## 4. Martian saline assemblages

Thermodynamic simulation of evaporation yields *osmotic coefficient* (calculated with Pitzer equations)



Water activity is proportional to the *osmotic coefficient*

$$\ln a_{H_2O} = \frac{\phi \left( \sum v_i m_i \right) M_w}{-1000}$$

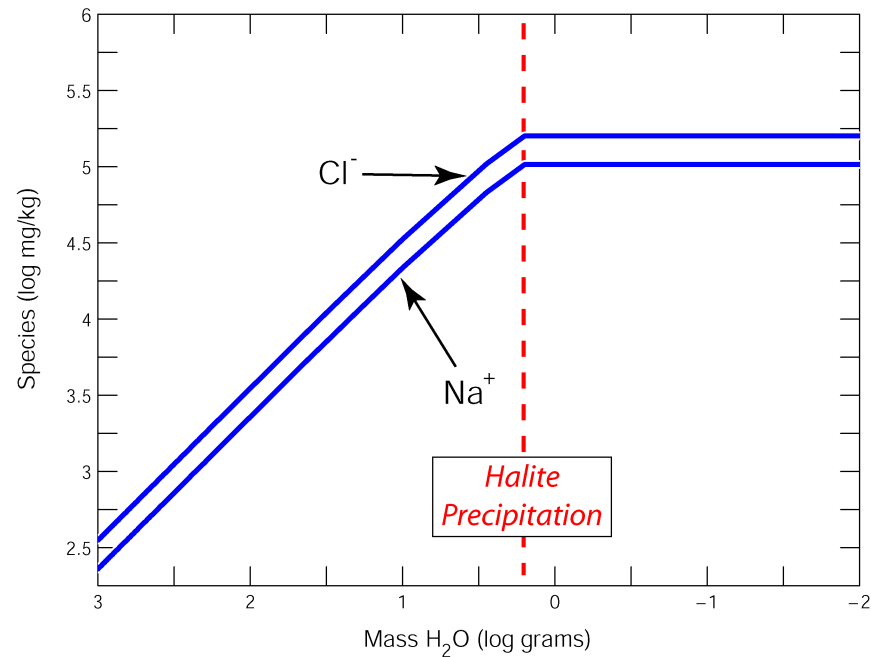
**Goal:** For a martian water, calculate  $a_{H_2O}$  at the point of saline mineral precipitation



# Mineral Precipitation and $a_{H_2O}$

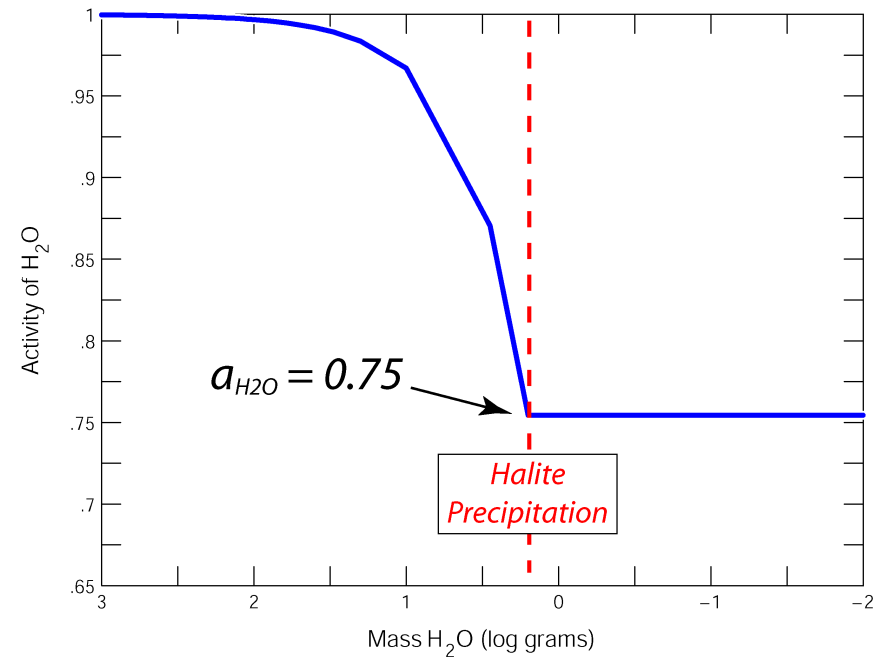


**Aqueous Concentrations**

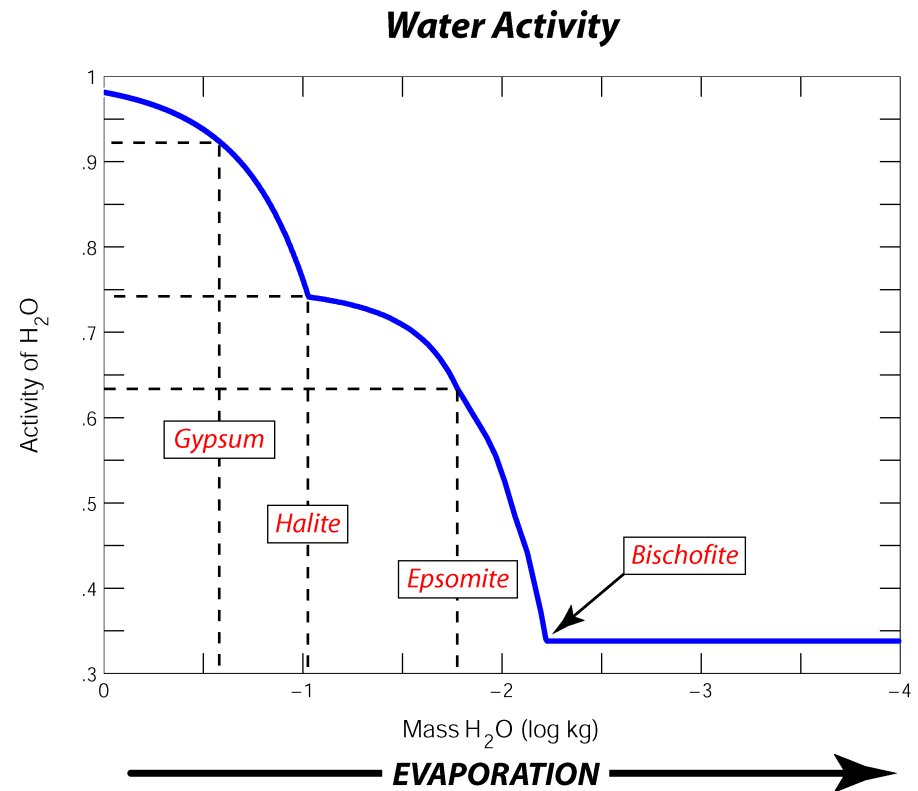
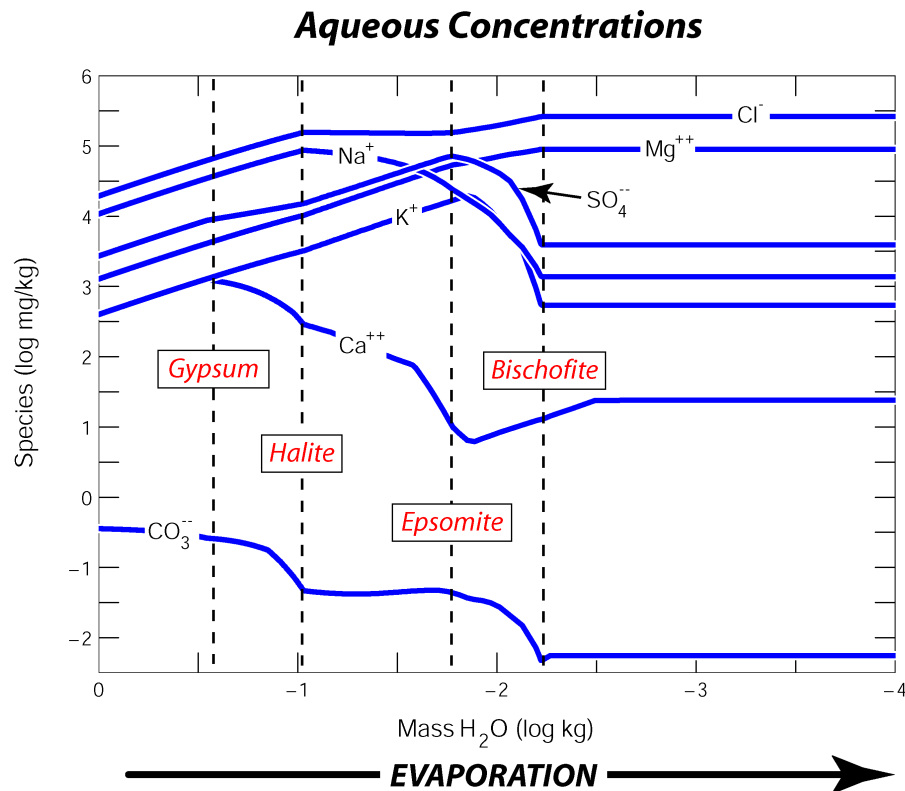


Evaporation →

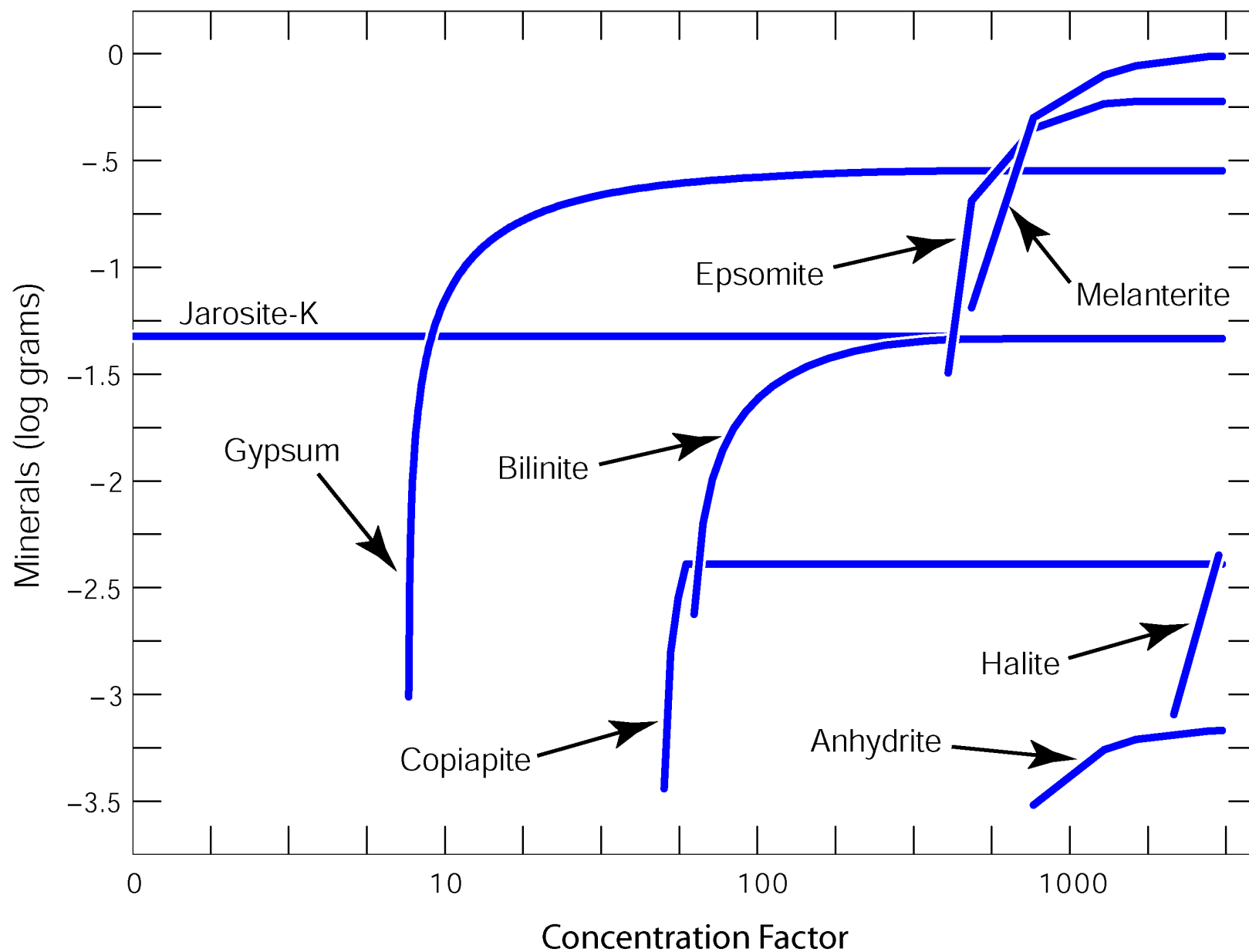
**Water Activity**



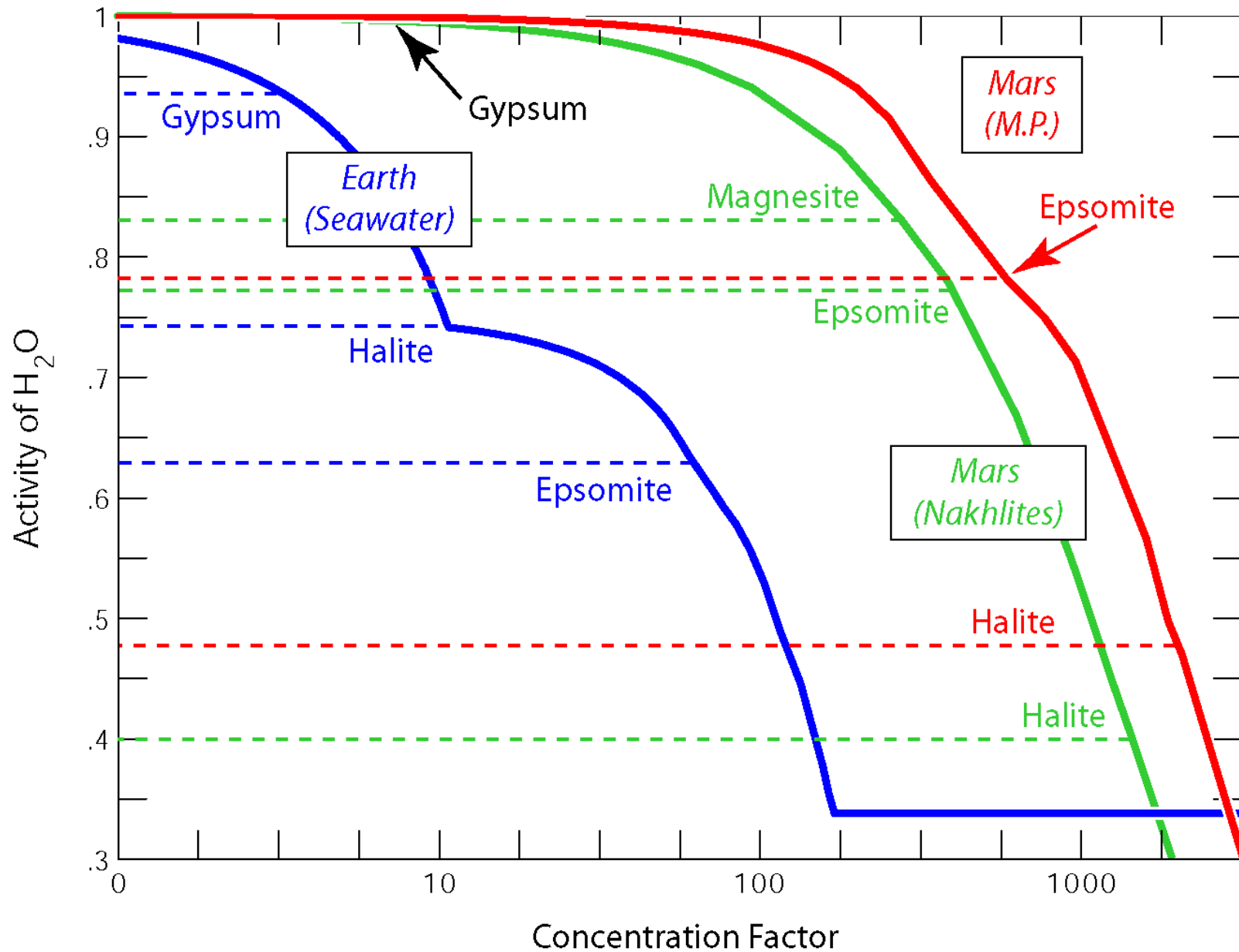
Evaporation →



# *Meridiani Planum Evaporite Minerals*



# Water Activity on Mars





**"London", Sol 149**

**Hematitic  
Nodule**

**Cementation**

**Crystal molds**

**5 mm**

***During groundwater diagenesis:***

- Selective mineral dissolution*
- Water at Mg-sulfate saturation*



# $a_{\text{H}_2\text{O}}$ : General Mineralogical Trends



- **Chlorides reflect distinctly low  $a_{\text{H}_2\text{O}}$  ( $<0.50$ )**
  - Function of sulfate vs. chloride solubility
  - Insensitive to  $\text{SO}_4/\text{Cl}$  ratio of initial water
- **Gypsum & carbonates are “insoluble” & reflect high  $a_{\text{H}_2\text{O}}$  ( $\sim 0.95$ )**
- **All Mg-,  $\text{Fe}^{2+}$ -sulfates reflect low  $a_{\text{H}_2\text{O}}$  ( $\sim 0.78$  and lower)**
- **$\text{Fe}^{3+}$ -sulfates (exclusive of jarosite & schwertmannite) reflect both low  $a_{\text{H}_2\text{O}}$  and low pH**
  - Include ferricopiapite, copiapite-group minerals, rhomboclase, etc.



# Low $a_{\text{H}_2\text{O}}$ : A Challenge for Life on Ancient Mars



- Distinction between *originating in* & *adapting to* low  $a_{\text{H}_2\text{O}}$

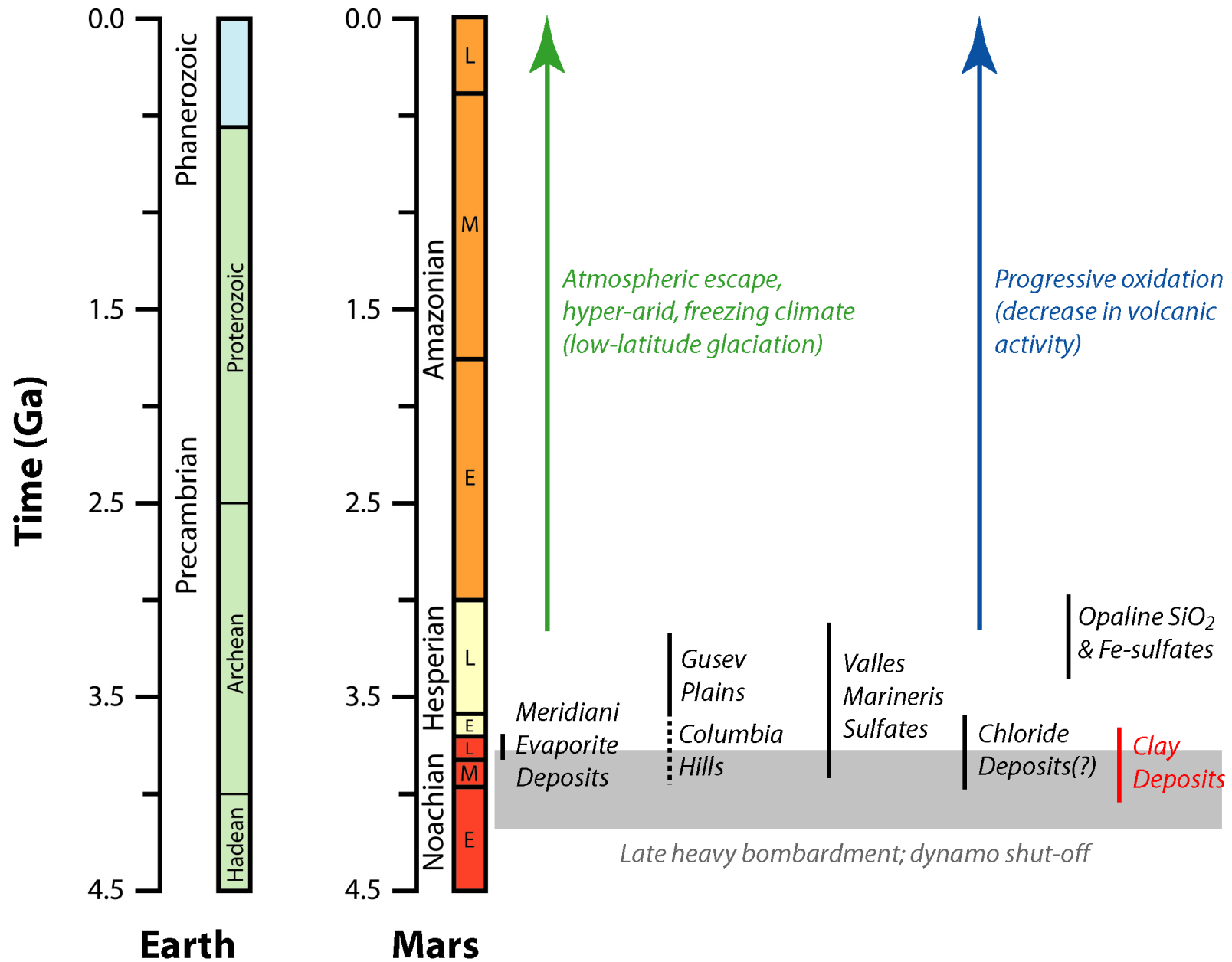
## *Selected Water Activity Values*

Epsomite at Meridiani Planum	0.78
Halite at Meridiani Planum	0.51
SNC Meteorite Brines	0.40
Paso Robles Soil Brines	0.61
Limit for most organism growth	~0.90
Limit for most extremophilic fungi & archaea	~0.75
Effective "habitability limit" ( <i>X. bisporus</i> )	0.61

- Halo-tolerance/philism is evolutionary
- Low  $a_{\text{H}_2\text{O}}$  and pH prohibit pre-biotic reactions
  - There must be numerical limits & they provide useful benchmarks
- Where are the dilute fluids?
  - Are we seeing snapshots as Mars evaporated to dryness?
  - Is this representative of  $\text{H}_2\text{O}$ -limited processes?
- Window of habitability was short and occurred early



# Relative Timing





# Origin, Evolution & Preservation



## *On a local/regional scale:*

- **Need Favorable “pre-biotic” chemistry**
  - Reducing conditions
  - “Mild” pH
  - Highest possible  $a_{\text{H}_2\text{O}}$
- **Maximum temporal availability of water**
  - Sustained versus episodic
- **Optimal preservational (post-depositional) characteristics**
  - *Less water exposure*
- *In other words: go to where life grabbed a foot-hold & was pickled*



# Optimal habitability & preservation: An Example



## Sites capturing a phyllosilicate → sulfate transition

- Gale crater, S. Meridiani, Miyamoto
- **Phyllosilicate-dominated strata: Habitable chemistry**
  - Higher  $a_{\text{H}_2\text{O}}$  (Generally)
  - Reducing (Fe-phyllosilicates)
  - Circum-neutral pH
  - Prolonged water availability
- **Sulfate-rich strata: Diverse preservation potential**
  - Morphology, isotopic signatures, etc.
- **Capturing the transition:**
  - How did chemistry & climate change?
  - How did life respond?
  - The essence of our understanding of the martian surface





# Maximizing Habitability: Syn-depositional Characteristics



## Water Activity

Good	Bad
Phyllosilicates <sup>a</sup>	Mg-sulfates (all)
Gypsum	Fe <sup>2+</sup> -sulfates
Carbonates	Na, K-sulfates
	Chlorides (all)
	Fe <sup>3+</sup> -sulfates <sup>b</sup>

## Redox

Good	Bad
Fe <sup>2+</sup> -phyllosilicates <sup>c</sup>	Fe <sup>3+</sup> -sulfates
Siderite	Fe <sup>3+</sup> -oxides

## pH

Good	Bad
Phyllosilicates	Fe <sup>3+</sup> -sulfates <sup>b</sup>
Gypsum <sup>d</sup>	"Ochreous" Fe <sup>3+</sup> -sulfates <sup>e</sup>
Mg-sulfates <sup>d</sup>	Fe <sup>2+</sup> -sulfates <sup>f</sup>

## Temporal availability of water\*

Good	Bad
Phyllosilicates	--

### NOTES:

<sup>a</sup> In general occur in dilute waters. Many smectites form in saline conditions, thus cannot as yet quantify a  $a_{H_2O}$

<sup>b</sup> Fe<sup>3+</sup> - sulfates exclusive of "ochreous" phases; include copiapites, rhomboclase, etc. These minerals require both low  $a_{H_2O}$  and very low pH to form

<sup>c</sup> Generally require reducing conditions. In addition, Fe<sup>3+</sup> - smectites may only form through the oxidation of Fe<sup>2+</sup> -precursors, suggesting they originally require reducing conditions

<sup>d</sup> These phases alone cannot constrain pH; they are pH-independent

<sup>e</sup> Include jarosite and schwertmannite; they are relatively insoluble but need acidic pH to form

<sup>f</sup> Do not strictly require low pH, but acidic pH favors their formation and stability through suppression of oxidation kinetics by O<sub>2</sub> (g)

\* Much of these constraints may come from sedimentology & in situ textural analysis in addition to geomorphology